HYDROPYROLYSIS - POTENTIAL FOR PRIMARY
UPGRADING OF TAR SAND BITUMEN

J. W. Bunger, D. E. Cogswell, R. E. Wood
and A. G. Oblad

Department of Mining and Fuels Engineering
320 WBB, University of Utah
Salt Lake City, Utah
84112

INTRODUCTION

Upgrading of high molecular weight, residual materials
is becoming increasingly important as a result of scarcity
of lighter feedstocks. Conversion processes for residual
materials must contend with high heteroatom content, low
volatility (high molecular weight), high aromaticity and
high metals content not encountered to the same degree in
lighter feedstocks. These characteristics result in higher
process costs and typically lower conversion and yield of
desired products. As yield and conversion efficiency become
more important, conventional techniques, e.g. coking, may
prove economically unacceptable, especially for primary
upgrading of bitumens or black oils.

Hydropyrolysis is a process for thermal cracking in the
presence of hydrogen. This process has been shown to drama-
tically improve the yields of liquid and gaseous products
compared to coking.[1-4] It does not rely on heterogeneous
catalysts but requires elevated pressures. Through model
compound work[5] and characterization and processing of high
molecular weight tar sand bitumen, an understanding of the
chemistry of this reaction is beginning to emerge. This
paper reports our latest results and hypothesis and the
general reactions which may be occurring. The implication
of the reaction pathways to the suitability of various
feedstocks for hydropyrolysis is also discussed.

EXPERIMENTAL

Elemental Analysis and Physical Properties

Elemental analysis was accomplished by conventional
microanalytical techniques in a commercial testing labora-
tory. Densities were measured on Mettler/Paar digital
density meter, model D.M. 40. Average molecular weights
were determined by VPO in benzene. Simulated distillation
was accomplished using a 1/4" by 18" column of 3% dexsil 300
on chromosorb W, programmed from -30° to 350° C at 10°/minute

with a 4 minute hold at 350° C. The detector was a flame
ionization detector maintained at 400° C. The percent
nondistillable was determined by use of an internal stan-
dard, an equal volume mixture of C_9 to C_{16} n-alkylbenzenes.
(See also references 6,7)

Hydropyrolysis Process

Two hydropyrolysis reactors were used in this study.
Feeds A and B were processed on a reactor consisting of a
coiled stainless steel tube 3/16" i.d. x 236" long. This[1]
reactor has been previously described by Ramakrishnan.
Feed C was processed in a reactor originally developed for
short residence time coal liquifaction. This reactor also
consists of coiled stainless steel tubes 3/16" i.d. The
length of this tube system can be varied from 20 to 120 [8]
feet, and has been previously described by Wood, et. al.
Average residence times were calculated from the volumetric
flow rates and the reactor volume at process conditions.

RESULTS

Feedstocks for hydropyrolysis processing were derived
from Uinta Basin, Utah, tar sand deposits. Three differing
feedstocks were used for which elemental analysis and phys-
ical properties are given in Table 1. While the carbon-type
chemical structure of these feedstocks is probably similar,
some important differences are noted. Feed B is of the
highest molecular weight, carbon residue, and viscosity and
lowest in API gravity and volatility. Elevated temperatures
of 100-150° C are required to pump this material. Feed C is
the lightest of the three with Feed A of intermediate quality.
These feeds represent a range of properties among heavy
oils.

These materials were processed by hydropyrolysis under
varying conditions of space time, residence time, tempera-
ture, and pressure. The general effect of these variables[9]
on process results has been previously reported. Higher
temperatures and longer residency times contribute sensi-
tively to higher gas production. Representative results
attained at conditions determined to be operable for 1-2
hour run times are given in Table 2.

Results show virtually 100% conversion of feedstocks to
liquids and gases. Ammonia, hydrogen sulfide and water were
inferred from the material balance on the respective hetero-
atoms and direct analysis of these compounds were not
conducted. The values shown in Table 2 were used to cal-
culate the hydrogen consumption. Hydrogen consumption is
not underestimated by the method of calculation[9] and is

TABLE 1

Elemental Analysis and Physical Properties of Feedstocks

PROPERTY	FEED A	FEED B	FEED C
Carbon (wt %)	86.2	86.3	86.7
Hydrogen	11.3	11.1	11.6
Nitrogen	1.1	0.8	0.7
Sulfur	0.4	0.35	0.5
Oxygen	0.9	1.4	<0.5
H/C atomic	1.56	1.53	1.59
Specific gravity 20/20	0.981	1.003	0.959
API gravity	12.7	9.5	16.0
Average M.W. (VPO)	713	778	410
Conradson Carbon Residue	9.1	14.1	6.8
% distillable below 530° C	44	34	69
Viscosity KP 77°F .05/sec	69	1500	3.9*

*shear = 200 sec^{-1}

modest considering the effect on yields. Calculations of
hydrogen requirements reveal that a hydropyrolysis plant
could easily operate in hydrogen balance by steam-reforming
methane gas produced.

Characteristics of hydropyrolysis liquid products are
given in Table 3. Only modest improvement has been made in
the H/C ratios and heteroatom removal, but notable improve-
ments have been made in physical properties compared to the
feed material. Average molecular weights of A and B have
been reduced in half and viscosities have been reduced by 4
to 5 orders of magnitude. The properties given in Table 3
suggest that a synthetic crude oil has been produced which
is amenable to conventional refining. Based on the obser-
vation that olefin production is inhibited by hydropyroly-
sis, it is anticipated that hydropyrolysis liquids will be

TABLE 2

Representitive Results of Hydropyrolysis

Process Conditions

	Product A	Product B	Product C
Temperature °C	525	500	525
Pressure (psig)	1500	1800	1800
Average residence time (sec)	18	30	5
Space velocity (LHSV)	1	1	1

Yields

	Product A	Product B	Product C
Weight % gases	27.3	27.3	12.8
liquid	73.7	73.9	85.6
residue	*	*	2.1
NH_3	0.61	0.38	0.1
H_2S	0.21	0.13	0.3
H_2O	0.79	1.15	-
	102.6	102.9	100.9
Hydrogen consumption (wt %)	2.6	2.9	0.9
(scf/bbl)	1600	1800	600

* Residual material for those runs was counted as liquids.

more stable for storage, transportation, or distillation than coker distillates.

169

TABLE 3

Characteristics of Hydropyrolysis Liquid Products

	Product A	Product B	Product C
Carbon	86.8	86.9	86.2
Hydrogen	11.4	11.4	11.6
Nitrogen	0.8	0.7	0.7
Sulfur	0.3	0.3	0.2
Oxygen	0.3	0.50	1.20
H/C atomic	1.56	1.56	1.61
Specific gravity 20/20	0.903	0.967	0.920
API gravity	25.2	14.8	22.3
Average MW (VPO)	321	352	312
% distillable below 530°C	85	68	97
Viscosity 77°F cp,	8.1	7000	246

DISCUSSION

The general reaction mechanism for hydropyrolysis follows free radical chemistry. Free radical initiation most likely proceeds through unimolecular bond scission
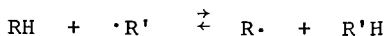
$$RR' \; \underset{\leftarrow}{\rightarrow} \; R\cdot \; + \; \cdot R'$$
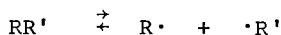
or bimolecular single atom transfer reaction to an unsaturated bond

$$RH \; + \; C=X \; \underset{\leftarrow}{\rightarrow} \; R\cdot \; + \; \cdot CXH$$
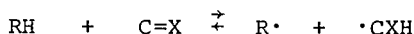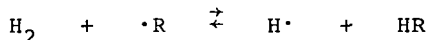
where X is most likely carbon or oxygen. (see reference 9 for arguments supporting this reaction)

Free radical propogation reactions proceed through transfer of hydrogen or other radical as:

$$RH \; + \; \cdot R' \; \underset{\leftarrow}{\rightarrow} \; R\cdot \; + \; R'H$$

Perhaps the most important reaction occuring during hy-

dropyrolysis is participation of hydrogen in this propaga-
tion reaction as follows:

$$H_2 \quad + \quad \cdot R \quad \underset{\leftarrow}{\rightarrow} \quad H\cdot \quad + \quad HR$$

Shabtai, et. al.[5] have postulated this reaction in
the hydropyrolysis of n-decane. An activation energy of 14-
15 kcal/mol is estimated on the basis of thermochemical
data[10,11].

The significance of this reaction is to increase the
relative effects of free radical saturation compared to β-
scission.[5] Thus, a dramatic decrease in ratio of olefin
to saturates is observed as a result of hydrogen participa-
tion. Also, the dilution of hydrocarbon species with hydro-
gen reduces the relative effect of second-order molecule-
molecule reactions. As a result, dehydrogenation reaction,
condensation reactions, and polymerization reactions are all
inhibited by the high partial pressure of hydrogen, or
indeed, light hydrocarbon gases.

Free radical termination may involve hydrogen radicals
to a large extent as radical-radical recombination

$$R\cdot \quad + \quad \cdot R' \quad \underset{\leftarrow}{\rightarrow} \quad RR'$$
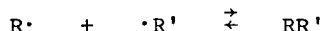
is again inhibited by the presence of hydrogen-rich gases.
The production of hydrogen radicals during hydropyrolysis
raises the prospect of hydrogeneration or hydrogenolysis
reactions. The contribution of these possible reactions
(probably minor) can only be inferred from the results of
hydropyrolysis where the average number of rings in the
aromatic nucleii appears to be reduced.

The effects of hydrogen on pyrolysis of bitumen are ob-
vious when compared with coking at 525° C which exhibits
yields of 4% gas, 83% liquid and 13% coke for feedstock A.
Clearly, the formation of coke has been severely inhibited
while considerable quantities of gas are produced. Consi-
dering that the amount of gas produced is closely related to
the amount of hydrogen consumed, optimum conditions will be
those which can effect the greatest molecular weight reduc-
tion without attendent high gas production. Shorter resi-
dence times than those achievable on the present equipment
may afford this objective.

Preliminary estimates of capital costs for hydropyrolysis
reveal an investment of about $3000/daily bbl capacity will
be required. This is considerably less than the investments
of approximately $6000/daily bbl capacity required for
coking/ hydrotreating necessary for the Syncrude plant in

Alberta, Canada. This advantage accrues partially from the fact that Uinta Basin bitumen is lower in total heteroatoms, especially sulfur, than Athabasca bitumen. Also, the hydro-pyrolysis oil is not as light as the synthetic crude pro-duced by Syncrude. The economic projections never-the-less reveal that for low sulfur, highly naphthenic bitumen, that hydropyrolysis may be an attractive alternative to coking.

SUMMARY

Hydropyrolysis promises to be a process for reducing molecular weight of residual material without the formation of coke, the use of catalysts or an inordinantly high con-sumption of hydrogen. Estimations of capital costs appear to be competitive with a coking/hydrotreating sequence. Ad-ditionally, hydropyrolysis affords 10-15% improved yield over coking/hydrotreating and this factor will have a signi-ficant impact on the economics of the recovery steps.

Hydropyrolysis gains its attractiveness principally through the inhibition of second-order hydrocarbon-hydro-carbon reactions relative to first order cracking reactions. Hydropyrolysis is, therefore, predicted to be most useful for processing of very high molecular weight feedstocks of moderate aromatic character. Naphthenic feedstocks are particularly benefited from the inhibition of dehydrogen-ation reactions.

REFERENCES

1. Ramakrishnan, R: Ph.D. Dissertation, Dept. of Fuels
      Engineering, Univ. of Utah (1978), 143 pp.
2. Bunger, JW, et. al.: ACS Petr Div Prepr, 23(4):98-109, 1978.
3. Bunger, JW, et. al.: ACS Petr Div Prepr, 24(4):1017-1027, 1979.
4. Pruden, BB et. al.: Can Chem Proc, 61:37-38, 1977.
5. Shabtai, J, et. al.: Chap. 18 in Advances in Chemistry
      Series (183), Oblad, AG, et. al. (eds), ACS, pp. 297-328, 1979.
6. Poulson, RE, et. al.: Analysis Instrumentation, Instrument
      Society of America, 10:193-200, 1972.
7. Bunger, JW, et. al.: Fuel, 58(3):183, 1979.
8. Wood, RE, et. al.: Ind Eng Chem, Process Res Dev, Vol. 15,
      No. 1, 1976.
9. Bunger, JW: Ph.D. Dissertation, Dept. of Fuels Engineer-
      ing, Univ. of Utah (1979), 217 pp.
10. Bensen, SW: "Thermochemical kinetics"; Wiley, NY, 1976.
11. Rosenstock, HM, et. al.: J Phys Chem Ref Data, 1977,
      6 (suppl. 1), pp. I-774-I-783.